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A New Method for the Production of Tetranitroglycoluril From Imidazo-[4,5-*d*]-Imidazoles With the Loss of Dinitrogen Oxide

by William M. Sherrill and Eric C. Johnson

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14. ABSTRACT A new method for the preparation of tetranitroglycoluril (TNGU) (also known as Sorguyl), is described in which imidazo-[4,5-d]-imidazoles are nitrated with the elimination of dinitrogen oxide (N_2O) to generate TNGU. This method of TNGU synthesis results in material that is less sensitive than material produced via alternative routes.						
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Contents

List of Figures

List of Tables

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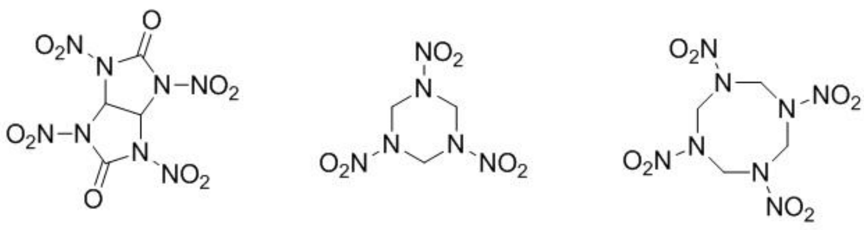
1. Introduction

Tetranitroglycoluril[*] (TNGU) **1** is a powerful high explosive that was first publicly described in the 1970s by the French (*1–3*). This material, with a density of 2.01 g/cm^3 and heat of formation (ΔH_f) of 50 kJ/mol makes it a powerful high explosive similar to the standard military explosives 1,3,5-trinitroperhydro-1,3,5-triazine (RDX, **2**) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX, **3**) (*4*) (figure 1).



1
TNGU

2
RDX

3
HMX

Figure 1. Structures of high explosives TNGU, RDX, and HMX.

Compound **1** has several undesirable characteristics that have impeded its adoption into military formulations. The first of these is its inherent water lability. The dinitrourea moiety present in the molecule readily hydrolyzes even on exposure to atmospheric moisture. This means formulations containing TNGU will rapidly degrade upon exposure to normal atmospheric conditions (*5*). While this feature is usually detrimental in an explosive, TNGU containing formulations are being investigated for use in potential self-remediating munitions to lessen the hazards associated with unexploded ordinance (UXO) (*6*).

Another detrimental feature of TNGU is the inherent sensitivity of the material that is synthesized and isolated according to literature procedures (*6*). TNGU as isolated using these methods has a 50% initiation (H_{50}) value for impact sensitivity of 4.10 inches (in) while RDX and HMX are 9.08 in, respectively. Additionally, TNGU has a friction measurement of 54 Newtons (N) while RDX and HMX both are approximately 120 N. Taken together, both of these numbers place TNGU in a category of materials that are usually deemed too sensitive to handle or formulate.

[*] Also known as Sorguyl.

Recent attempts to rectify both the hydrolytic instability and the sensitivity of TNGU through substitution of the bridgehead hydrogens resulted only in material that was energetically less powerful and still of comparably sensitivity and stability (*7*). This led to the idea of using substitution of the oxygen from the carbonyl position in the dinitrourea moiety as an additional means of potentially tuning both the sensitivity and the hydrolytic instability of the molecule (figure 2). To this end, several different imidazo imidazoles **4-6** were prepared using known literature procedures (*8*) and then attempts were made to further nitrate them to produce a novel material **7** (figure 3). Both **5** and **6** are noted in the Kony paper (*8*) to be explosives in their own right; however, complete sensitivity analysis was never reported. A separate report details the synthesis of these materials and found that while both **5** and **6** may be considered energetic materials, both are significantly less sensitive than RDX (*9*).

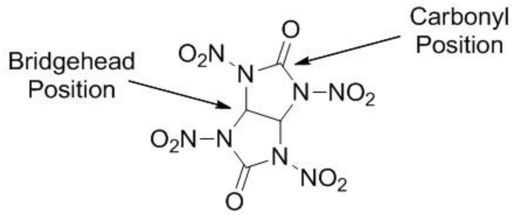
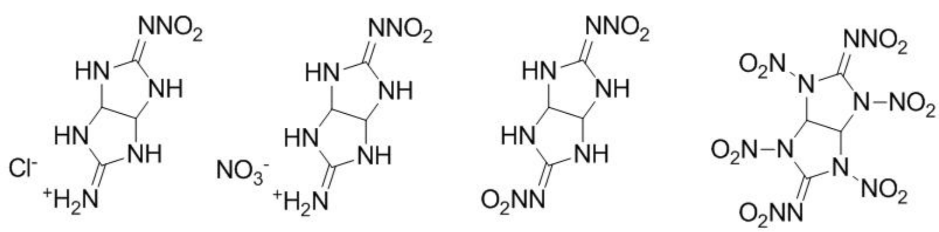


Figure 2. TNGU showing location of bridgehead and carbonyl positions.



4 5 6 7

Figure 3. Structure of starting material imidazo imidazoles 4-6 and target 7.

2. Computational Analysis

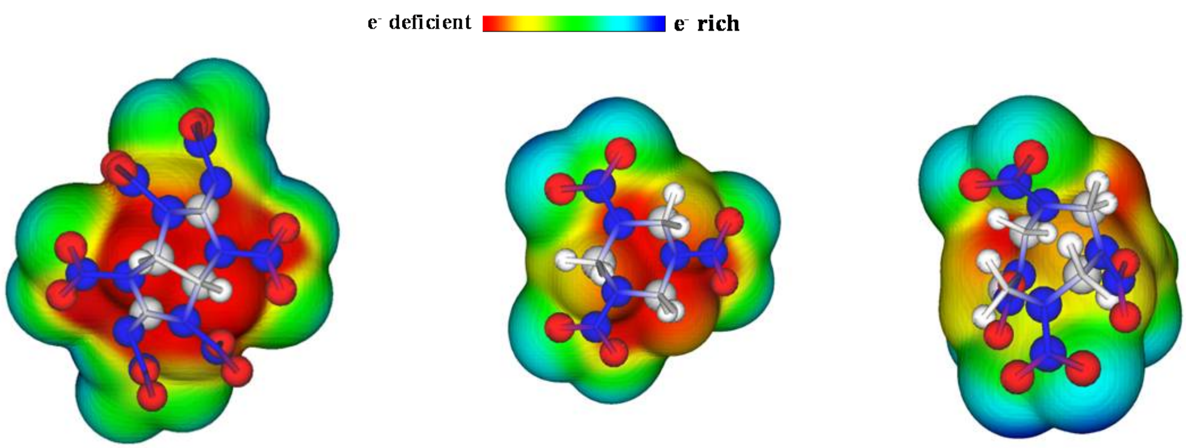
Having determined the sensitivity of these materials, further nitration was then attempted in an effort to synthesize **7**. The target **7** is predicted by quantum mechanical models developed by Rice (*10–14*) to have a density of 2.032 g/cm^3 and a ΔH_f of +617.01 kJ/mol. From these numbers, the predicted performance of this material exceeds HMX by almost 30% making it a highly desirable target (table 1).

Table 1. Performance predictions from Cheetah 7.0 (*4*).

Substance	ρ[a]	ΔH_f (kJ/mol)	P_{cj}[d] (GPa)	D_v[e] (km/s)	ΔH_d[f] (kJ/mL)	OB[g] (%)
7	2.03[b]	617.01[b]	42.51	9.621	12.17	+11.70
TNGU[c]	2.01	50.0	41.77	9.566	11.78	+4.97
RDX[c]	1.816	70.01	33.46	8.862	10.42	–21.61
HMX[c]	1.90	75.02	37.19	9.246	11.00	–21.61

[a]Density. [b]Predicted using the methods of Rice (*10–14*). [c]ΔH_f and density numbers obtained from Cheetah 7.0 database. [d]Chapman-Jouguet pressure. [e]Detonation velocity. [f]Heat of detonation. [g]Oxygen balance.

Using visualization software the theoretical electron surface potential map (SPM) of **7** was examined for areas of large predicted electron buildup or deficiency. The areas of high-electron density in figure 4 are represented in blue, while areas of electron deficiency are shown in red. It is currently believed that molecules exhibiting large areas of charge separation are generally less stable than molecules with an SPM showing a well distributed surface charge. Upon examining the SPM of **7**, it can be observed that the center of the molecule exhibits a higher area of electron density as compared to RDX and HMX suggesting that **7** may be more sensitive.



7 **RDX** **HMX**

Figure 4. SPM of target material 7 compared to RDX and HMX.

3. Synthesis

With the predicted performance and sensitivity in hand, the synthesis of **7** was attempted from all three starting materials **4**, **5**, and **6**. None of the standard suite of acidic nitration conditions of 100% nitric acid (HNO_3), mixed sulfuric acid (H_2SO_4)/<98% HNO_3, and acetic anhydride (Ac_2O)/100% HNO_3 were found to be strong enough conditions to convert the lesser nitrated materials to the desired target. When subjecting materials **5** and **6** to >98% HNO_3, no reaction is observed; however, when using **4**, the material is recovered as the nitrate salt, **5**. All compounds

4-6 exhibit decomposition in mixed H_2SO_4/HNO_3 conditions and no products from these reactions were successfully recovered. Compounds **4** and **5** are both converted to the dinitro compound **6** when subjected to Ac_2O/HNO_3 conditions, but were unable to be nitrated further even with extended reaction times and heating. It was discovered that **4-6** can be further nitrated by employing a nitration mixture using trifluoroacetic anhydride (TFAA) in conjunction with HNO_3. In this case, when **4**, **5**, or **6** is dissolved in <98% HNO_3 and TFAA is added slowly, a white powder slowly precipitates over time with the evolution of gas bubbles. After several hours, the powder was isolated and analyzed to find the material was not **7** as anticipated, but rather TNGU. This was further confirmed by obtaining a nuclear magnetic resonance (NMR) spectrum showing perfect overlap of signals from a mixture of **1** prepared via the nitration of **4-6** and of TNGU prepared via the literature method (*6*). All three starting materials **4-6** yield TNGU as the product under the TFAA/HNO_3 conditions with reasonable yields although **5** consistently has product yields between 70% to 80% (table 2).

Table 2. Summary of nitration conditions and results.

Substance	**>98% HNO_3**	**>98% H_2SO_4/>98% HNO3**	**Ac_2O/<98% HNO_3**	**TFAA/<98% HNO_3**
4	**5**	Decomposes	**6**	**1**
5	No RXN	Decomposes	**6**	**1**
6	No RXN	Decomposes	No RXN	**1**

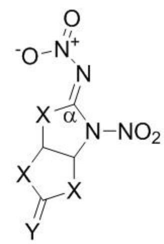
4. Mechanism

Of the myriad of possible scenarios, it is postulated that two are the most likely. The first being the α–carbon* of **7** is so electron withdrawn that the molecule is rapidly and completely hydrolyzed to TNGU on exposure to moisture. This theory was quickly dismissed by repeating the experiments using meticulously dried starting materials and glassware in conjunction with completely anhydrous reagents under an inert gas atmosphere. Workup was done by allowing the powder to settle to the bottom of the nitration mixture and decanting the mother liquor. The product was then washed extensively with anhydrous dichloromethane (DCM) and immediately analyzed. Analysis of the material obtained showed it to be identical to material isolated in the original experiments indicating that hydrolysis of **7** is not responsible for the formation of **1** under the reaction conditions or under workup.

The second scenario employs intra or intermolecular degradation with elimination of dinitrogen oxide (N_2O) as the driving force behind the formation of **1**. Once the material is subjected to the

* α designates the carbonyl carbon of the imidazo imidazole.

nitration conditions, it is plausible that each of the materials **4-6**, proceeds through an intermediate resembling **8** (figure 5). The α–carbon of this species is severely electron deficient making it highly susceptible to nucleophilic attack.

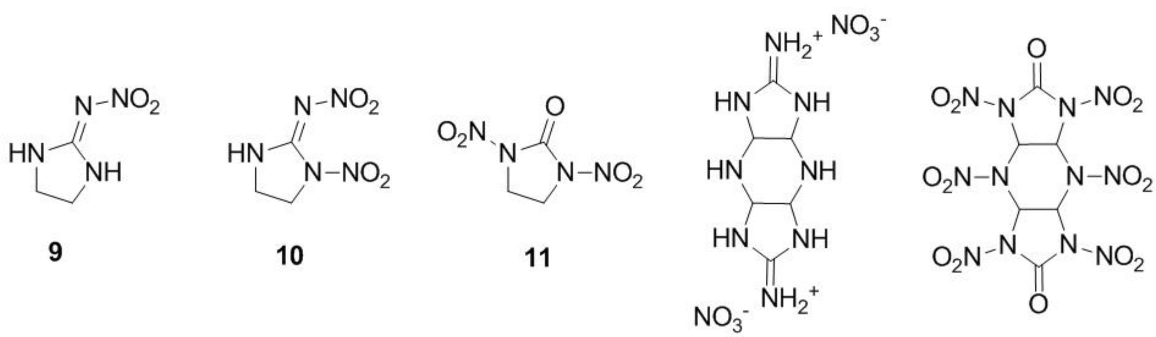


X = NH,NNO$_2$ Y = NH$_2^+$, NNO$_2$

8

Figure 5. Postulated intermediate in the formation of 1.

This type of reactivity with the elimination of N_2O has been documented previously by Wright and McKay (*15*) in their attempt to further nitrate **9** while only recovering **11** (figure 6). They proposed an intermediate **10**, which could easily rearrange under the nitration conditions with elimination of N_2O to ultimately form **11**. Additionally, this type of reactivity has been used in the synthesis of 2,6-dioxo-1,3,4,5,7,8-hexanitrodecahydro-1H,5H-diimidazo[4,5-b:4',5'-e] pyrazine (HHTDD) **13** starting from **12** (*5*).

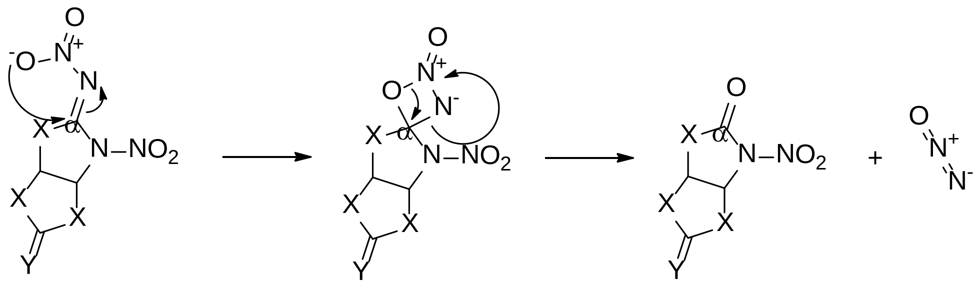


9 **10** **11** **12** **13** HHTDD

Figure 6. Literature examples of substrates believed to extrude N_2O.

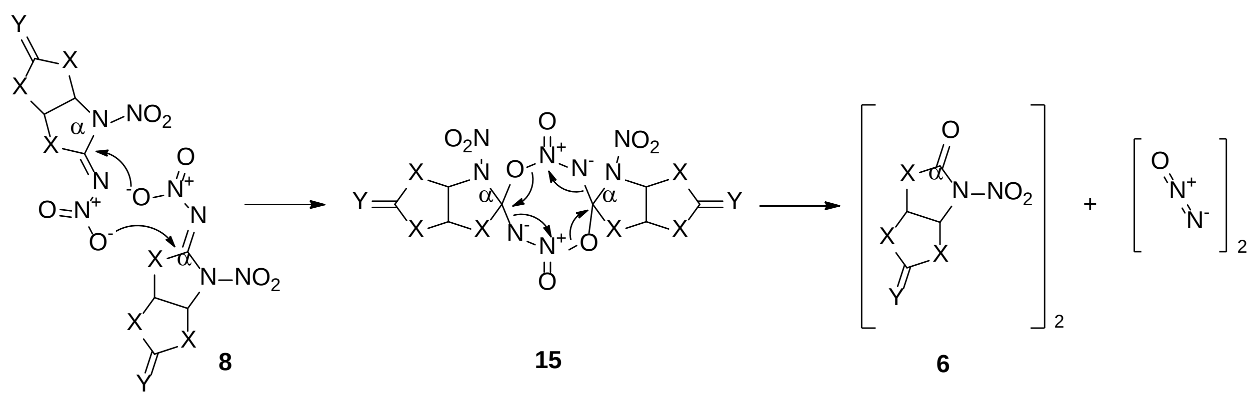
The intramolecular decomposition mechanism is envisioned to employ the oxygen of the nitrimino moiety as the nucleophile and then proceed through a four-membered intermediate **14**. (Scheme 1). The subsequent rearrangement of the four-membered cycle results in the liberation of N_2O and a nitrourea type species **6**. This mechanism is plausible whether the starting intermediate is a dinitro- or trinitroimidazo imidazole.

4.1 Scheme 1—Proposed Mechanism for the Intramolecular Decomposition and Extrusion of N_2O



Alternatively, the intermolecular mechanism starts from the same intermediate; however, it uses an additional molecule of **8** as the oxygen source (Scheme 2).

4.2 Scheme 2—Proposed Mechanism for the Intermolecular Decomposition and Extrusion on N_2O



There are two possible ways to test the plausibility of the degradation theory. The first is ^{18}O labeled HNO_3 to pinpoint the source of the oxygen nucleophile. This is prohibitively expensive due to the cost of ^{18}O labeled HNO_3. The second, and most feasible, is to monitor the headspace of the nitration mixture for the appearance of a higher than baseline concentration of N_2O. N_2O gas exhibits a very specific doublet in the infrared (IR) at approximately 2,235 cm^{-1}. Using headspace Fourier transform infrared (FTIR) spectroscopy it was possible to monitor the concentration of N_2O in the headspace of a nitration mixture without substrate present. This was used as the baseline for the subsequent experiments. The setup for the headspace monitoring experiment is shown in figure 7. For comparison, a spectrum of pure N_2O is available in the appendix of this report.

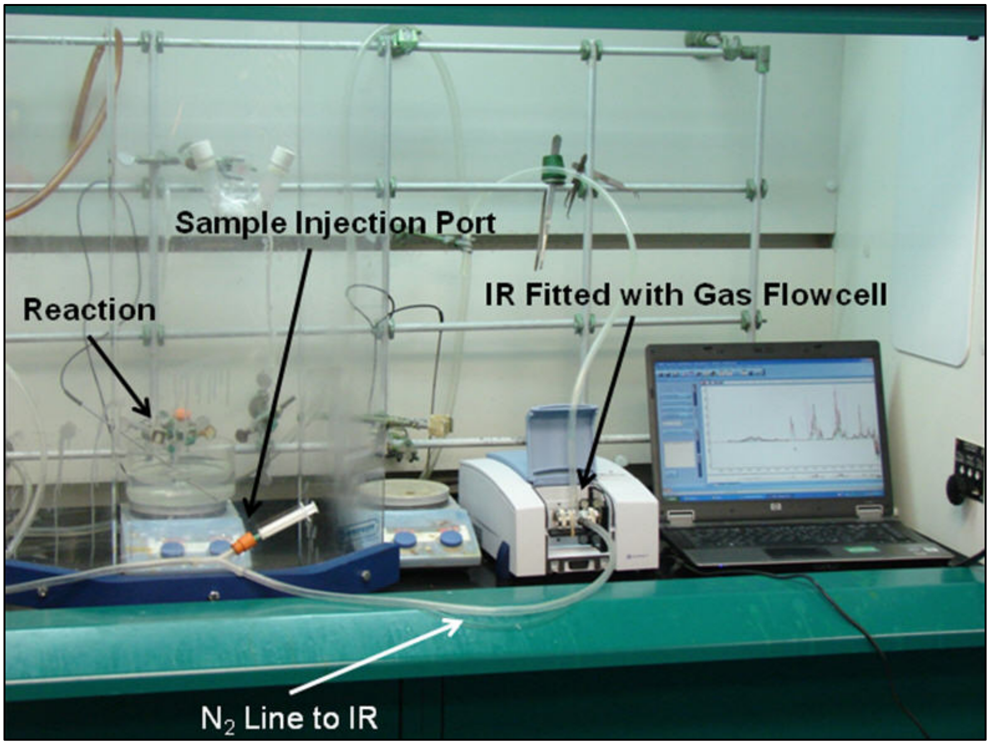


Figure 7. Reaction headspace FTIR monitoring setup.

The highest concentration of N_2O measured in the headspace of the baseline nitration mixture never exceeded 0.05 absorbance units (AU) indicating the amount of N_2O produced from the nitration mixture itself is minimal under the conditions used in the experiment. When glycoluril is added to the nitration mixture, the measured concentration of N_2O increases slightly; however, the maximum concentration still never exceeded 0.20 AU. When compounds **4**, **5**, or **6**, are subjected to the nitration conditions, the maximum concentration of N_2O observed in the headspace is more than five times higher than the maximum concentration observed for glycoluril (figure 8). The fact that TNGU is the only product recovered from the nitration of **4-6** together with those compounds exhibiting a maximum N_2O headspace concentration of 1.45 AU, a marked increase over reactions containing glycoluril, are strong indicators of a reaction mechanism similar to what is depicted in Scheme 1 and Scheme 2 is in operation.

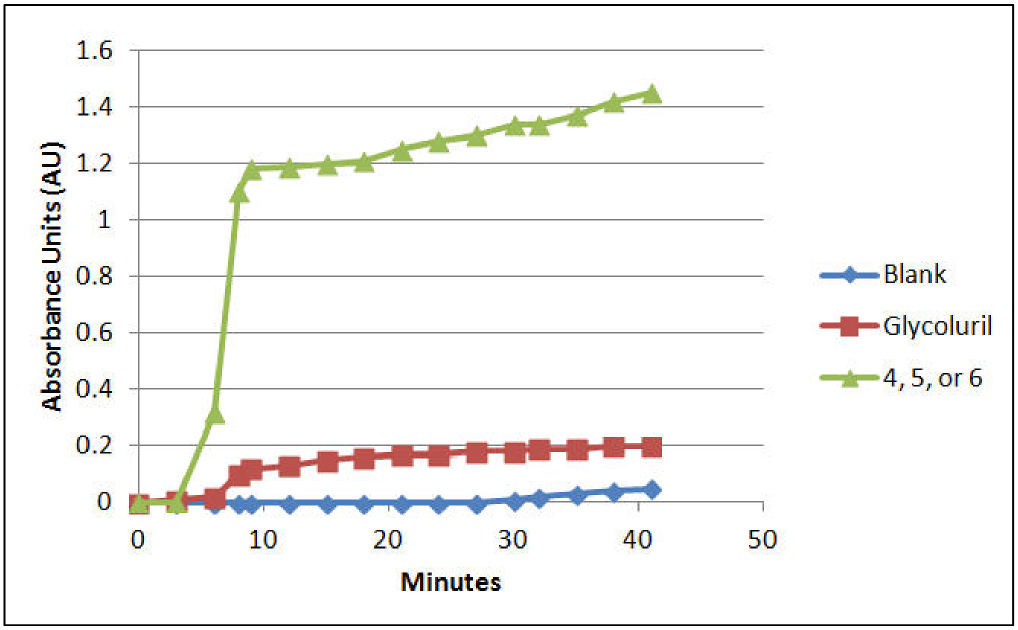


Figure 8. Concentration of N_2O in headspace of reactions over time.

5. Sensitivity

It is interesting to note that the sensitivity of **1** produced via the nitration of **4-6** with TFAA/HNO_3 is markedly improved over **1** produced using the literature (*6*) Ac_2O/HNO_3 nitration of glycoluril. As of yet, the reason for this increased stability is not completely understood although it is postulated that morphological differences between the materials may be responsible. TNGU produced via the (*6*) method has a drop height of 4.10 in on our impact testing apparatus while that produced via the TFAA method has a drop height of 11.07 in. The friction and electrostatic discharge (ESD) measurement between both samples remain comparable.

Table 3. Sensitivity data.

Substance	**Impact (in)**[a]	**Friction (N)**[b]	**ESD (J)**[c]
TFAA/HNO_3 **1**	11.07	70	3.25
Ac_2O/HNO_3 **1**	4.10	54	3.25
RDX	9.08	120	0.625
HMX	9.60	120	0.025

[a]H_{50} impact height determined on an apparatus using a 2-kg weight by the Langlie one-shot method (*16*). [b]Friction determined on a Julius Peter's BAM friction apparatus. [c]ESD determined using an ABL Laboratories ESD apparatus.

6. Experimental

H_{50} values for drop weight testing were determined using the Langlie one-shot method on a tester dropping a 5-lb weight from a maximum height of 60 in (*16*). Friction sensitivity measurements were determined on a BAM friction apparatus and ESD was determined using an ABL Laboratories ESD apparatus. NMR experiments were done using an Anasazi Instruments 90-megahertz (MHz) nuclear magnetic resonance (NMR). FTIR was obtained from a Brüker Alpha-T fitted with a 5-cm path length gas flow cell in the transmission module, or a diamond-attenuated total reflectance (ATR) module. Differential scanning calorimetry was conducted on a TA instruments Q10 or Q20 calorimeter. All chemicals were obtained from Sigma-Aldrich, St. Louis, MO, and were used as received.

Note: While these compounds were prepared without incident according the following procedures, these materials are energetic and should be prepared and handled cautiously by trained personnel.

Synthesis of 4-6

The syntheses of these compounds were carried out according to the methods detailed by Kony (*8*). These procedures were quickly and accurately reproduced to yield **4-6** and analysis of the resulting products matched the data given in his publication. Sensitivity analysis of these materials is available in a separate report (*9*).

Alternate preparation of 5

Kony originally prepared **5** by the action of 100% HNO_3 on the purified hydrochloride salt **4**. It was discovered that **5** is most easily prepared by taking the crude **4** obtained from the procedures described in the Kony report and dissolving it in 70% HNO_3. Once all the material was dissolved, it could be crash precipitated by pouring over ice followed by purification from dilute HNO_3 as described by Kony.

Synthesis of 1 from 4-6

Representative procedure from 4: 100 mg (0.45 mmol) of **4** was dissolved in 2 milliliters (mL) of 100% HNO_3 at 0 °C under an inert nitrogen (N_2) atmosphere. To this solution was added 2 mL of TFAA drop wise at such a rate as to keep the temperature of the solution below 10 °C. After the addition was completed, the reaction was allowed to warm to room temperature and stirred for 2 h at which point stirring was stopped and the precipitant was allowed to settle. The mother liquor was decanted and the residual solid was washed with anhydrous DCM (5 × 5 mL). The solid **1** was then dried under vacuum (10 torr) at ambient temperature for 2 h. The total amount of **1** recovered from this process was 0.701 g (0.22 mmol, 49%).

From 5: 1 was prepared from **5** according to the preceding representative procedure. The total amount of **1** recovered from 100 mg (0.40 mmol) of 5 was 104 mg (0.32 mmol, 80%).

From 6: 1 was prepared from **6** according to the representative procedure. The total amount of **1** recovered from 100 mg (0.43 mmol) of 6 was 0.892 mg (0.28 mmol, 65%).

Scale up to 2 g of 1 from 5: 2.027 g (8.16 mmol) of nitrate salt **5** was dissolved into 40 mL of 100% HNO_3 at 0 °C under an N_2 atmosphere. To this solution was added drop wise 40 mL of TFAA at a rate to keep the temperature under 10 °C. Upon completion of the addition, the material was allowed to warm to ambient temperature and stirring was continued for 2 h. After the time had elapsed, the suspension was cooled to 0 °C, stirring was stopped and the suspended solid was allowed to settle. The mother liquor was decanted and the remaining solid was washed with DCM (5 × 20 mL). The material was then vacuum dried (10 torr 20 °C) for 2 h. The total amount of **1** recovered from this process was 1.89 g (5.86 mmol, 72%)

Procedure for headspace analysis

The Brüker Alpha-T was fitted with the transmission module and in it was placed a 5-cm-long gas flow cell fitted with zinc selenide (ZnSe) windows. A sample injection port covered with a septum was fitted to the intake side of the gas supply line approximately 6 in prior to the cell. The exhaust of the cell was vented into the fume hood. N_2 carrier gas at 12 mL/minute (min) was flowed through the cell at all times while measuring the concentration of N_2O in the headspace. A background of pure N_2 was used and a sample of pure N_2O was injected into the cell to confirm the setup was functioning correctly. A 6-mL sample of the reaction headspace from a 100-mg scale reaction was injected and analyzed at 3-min intervals. The amount of N_2O present in the sample was determined by measuring the absorbance unit values for the N_2O peak of the doublet at approximately 2,235 cm^{-1}.

7. Conclusions

A new method for the synthesis of **1** has been discovered from materials other than glycoluril. This new method causes the substrates to lose N_2O during the nitration process and the product obtained via this new route is more stable to external insult than material produced according to traditional literature methods while still having analytics matching that of the material produced according to the literature procedures.

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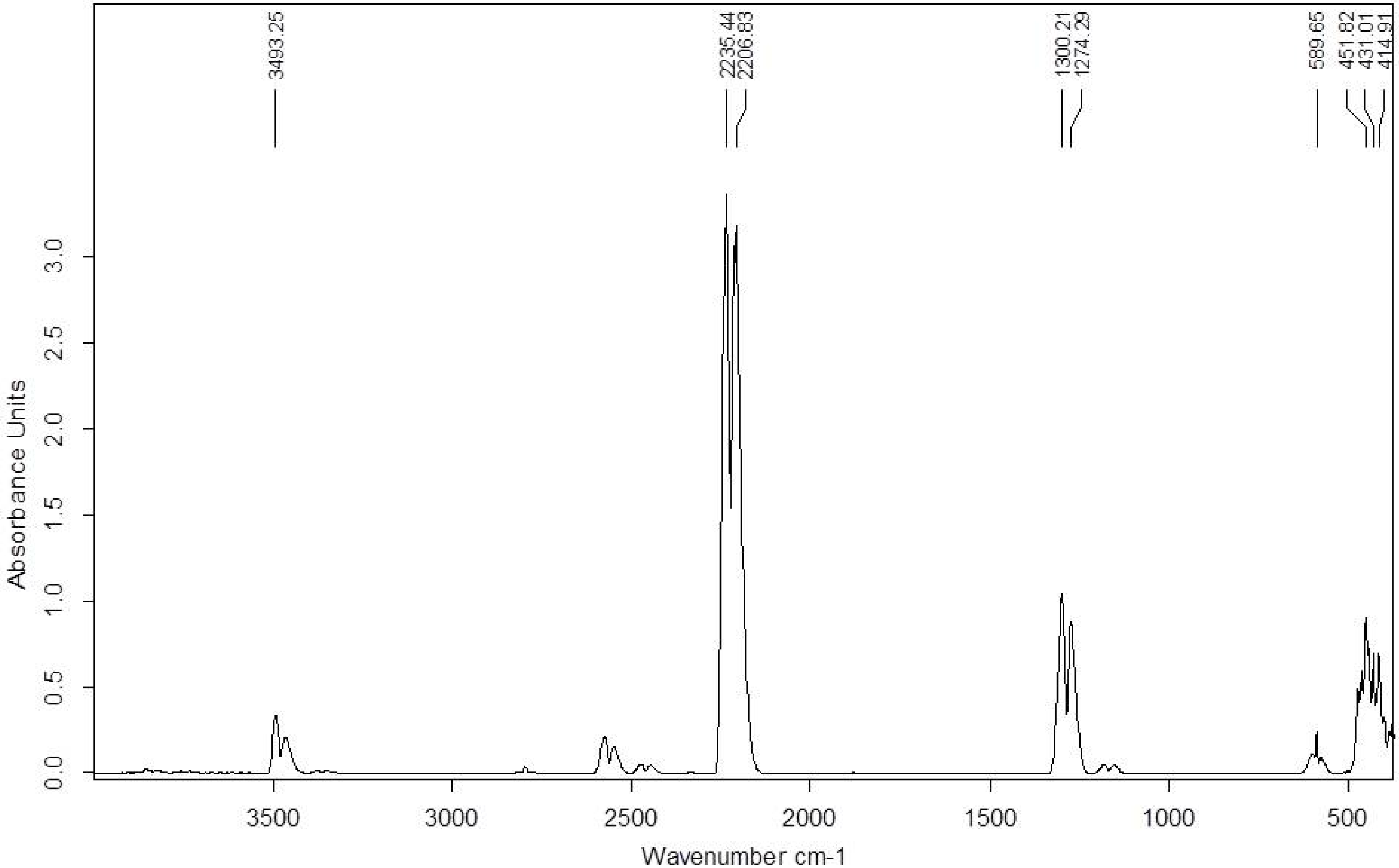
Appendix. FTIR Data

This appendix appears in its original form, without editorial change.



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Page 1/1

FTIR of N_2O

List of Symbols, Abbreviations, and Acronyms

Ac_2O	acetic anhydride
ATR	attenuated total reflectance
AU	absorbance units
DCM	dichloromethane
D_v	detonation velocity
ESD	electrostatic discharge
FTIR	Fourier transform infrared
H_2SO_4	sulfuric acid
H_{50}	50% initiation height
HHTDD	2,6-dioxo-1,3,4,5,7,8-hexanitrodecahydro-1H,5H-diimidazo[4,5-b:4',5'-e] pyrazine
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HNO_3	nitric acid
in	inch
IR	infrared
MHz	megahertz
min	minute
mL	milliliter
N	newton
N_2	nitrogen
N_2O	dinitrogen oxide
NMR	nuclear magnetic resonance
OB	oxygen balance
P_{cj}	Chapman-Jouguet pressure
RDX	1,3,5-trinitroperhydro-1,3,5-triazine

SPM	surface potential map
TFAA	trifluoroacetic anhydride
TNGU	tetranitroglycoluril
UXO	unexploded ordinance
ZnSe	zinc selenide
ΔH_f	heat of formation
ΔH_d	heat of detonation
α	designates the carbonyl carbon of the imidazo imidazole
ρ	density

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